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Supramolecular Oligourethane Gel with Multicolor Luminescence Controlled by Mechanically Sensitive Hydrogen-Bonding

Nan Jiang, Shi-Hao Ruan, Xing-Man Liu, Dongxia Zhu,* Bing Li,* and Martin R. Bryce*



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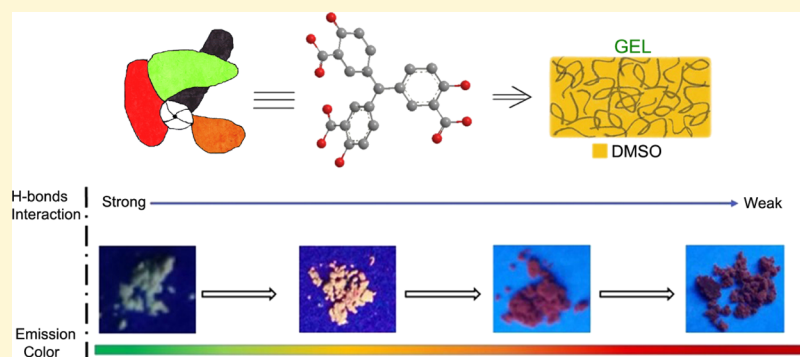
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ABSTRACT: We report a new type of mechanically sensitive multicolor luminescent oligourethane gel (OUA-gel). The conformation of the oligomeric chains can be controlled by changing the strength of hydrogen bonds. The optical properties of the oligomers are highly dependent on the conformations which vary in response to mechanical stresses and phase transitions. The design relies on the introduction of a single mechanical chromophore, aurintricarboxylic acid, with propeller-like, spatially crowded, and highly twisted conformations, and the presence of three carboxyl groups, which provide multidirectional hydrogen-bonding opportunities. Introducing dimethylsulfoxide (DMSO) as an additional H-bond acceptor molecule leads to a viscous OUA-gel which exhibits multiemission colors because of changes in the chain conformation within the matrix, which are induced by different strengths of H bonds. The conformation can be adjusted by mechanical force or temperature, both of which influence the H-bonding. The multifunctional and multicolored mechanochromism of the OUA-gel has great promise in sensing applications. The results represent a substantial step toward understanding the mechanism of polychromism in soft materials and the molecular design of advanced smart materials.

Mechanochromic materials change color when mechanical pressure is applied. They have great potential as smart materials, for example, as sensors, memory devices, and displays.^{1–5} A visual change in color can be induced by altering the chemical identity, intermolecular interactions, or orientation of chromophores under mechanical stress.^{6,7} Mechanochromic materials exist in various forms such as solutions, nanoparticles, solid powder, films, and gels.^{8–12} Among them, gels have advantages such as structural stability, processability, facile manufacturability, cost, and other practical issues such as being easily coated on the surface of a variety of substances, including metals, ceramics, and plastics.¹³ Therefore, gelators that can respond to mechanical stimuli are a great option for mechanochromic materials. Polymers/oligomers are particularly attractive in this field because their fluorescence spectra exhibit distinct vibronic bands, the intensity and wavelength of which are very sensitive to the chain conformation.^{14–17} However, reliable control of optoelectronic performance remains a challenge owing to the random nature of molecular

conformations, packing, and morphology of polymers/oligomers.¹⁸

The introduction of a mechanically active chromophore into a polymer backbone is an effective way to obtain mechanochromic materials.^{19–21} When mechanical force is applied, the chromophore is activated, causing a color change in the polymer/oligomer. However, the design of mechanical chromophores is challenging.^{22–27} Most of the reported materials change between two colors in response to mechanical stimuli and only a few exhibit multicolor changes (i.e., they show more than two colors in response to different types or different intensity of applied mechanical force) and they generally have complex structures.^{28–31} Therefore, the design

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and synthesis of multicolor mechanochromic/thermochromic materials is very important. The diversity of hydrogen-bonding motifs allows for tunable morphologies;³² the enhanced directionality of hydrogen-bonding is beneficial compared to ionic interactions.

Inspired by recent applications of hydrogen-bonding in polymers,^{33–38} we have now designed a multiple H-bonding supramolecular gel network, which has been realized via: (i) self-association of interchain multiple H-bonding interactions involving multicarboxy groups. (ii) Aurintricarboxylic acid with sterically crowded and very twisted conformations is a key subunit in the main chain. Meanwhile, no π – π stacking interactions occur between aromatic rings owing to the propeller-like conformations of the backbone, thus giving greatly enhanced emission. (iii) Addition of DMSO as an external cross-linking reagent acts as a H-bond receptor. Following these design features, multifunctional and thermochromic/mechanochromic soft materials based on oligourethane (OU) are achieved through a facile one-pot reaction. To the best of our knowledge, this is the first example of an OU derivative that exhibits multicolored emission through the application of mild mechanical force.

OUA-gel (Figure 1) is a polychromatic soft material which can distinguish mechanical stress from tension or grinding,

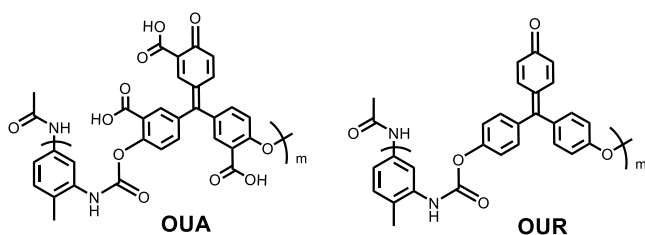


Figure 1. Structures of OUA and OUR.

showing fluorescence changes in response to different mechanical stimulation. There is a color change from green to yellow (grinding) or to red (tensile). The remarkable optical properties stem from the combination of six different types of hydrogen bonds, including the self-complementary H bonds of carboxyl groups, H bonds from urethane amide groups with carboxyl groups or carbonyl groups, and H bonds between the sulfoxide unit of DMSO molecules among the gel matrix with urethane amide groups or carboxyl groups. Thus, a dynamic physical cross-linked **OU-gel** network is constructed which depends only on H bonds. The network structure is adjustable, and upon different mechanical or temperature stimuli, there is

a rich multicolor response. Analysis of experimental results, coupled with H-bonding theory, demonstrated that a transition from amorphous to crystalline state is responsible for the optical response of the material. **OUA-gel** could find applications in sensitive shear and/or pressure sensors. **OUR-gel**, which lacks the carboxylic acid substituents, was studied as a model compound.

RESULTS AND DISCUSSION

OUA-gel was prepared by the reaction of aurintricarboxylic acid and tolylene-2,4-diisocyanate (TDI) in dimethylsulfoxide (DMSO) solvent. DMSO acts as a cross-linking agent. OUA became a sticky gel after a one-pot reaction for 8 h (Figure 1). **OUR-gel** was similarly prepared from rosolic acid. The detailed synthetic methods and proton nuclear magnetic resonance (¹H NMR) characterization are reported in the Supporting Information (Figures S1 and S2). The M_w values of 3162 and 2882 g mol^{−1}, for **OUA-gel** and **OUR-gel**, respectively, determined by gel permeation chromatography, established that the products are oligomeric, rather than polymeric.

In previous studies, we explored the self-assembling gelation behavior arising from interactions among amide, carbonyl, and sulfone groups in oligourethane derivatives.³⁹ In the present work, we observed the formation of **OUA-gel** at the molecular level by atomic force microscopy (AFM) (Figure S3). When the **OUA-gel** was diluted with DMSO to 0.1 M, well-defined pearl-like nanostructures (with a bead diameter of 100 nm) emerged in the solution. Interestingly, the magnified AFM images show that there is a tendency for pearl-like assemblies to combine end-to-end, finally forming entangled nanobelts (Figure S3c,d). We propose that hydrogen bonds are the major driving force during gelation behavior and studied these interactions in this gel system. As shown in the Fourier transform infrared (FTIR) spectra (Figure S4a,b), in contrast to OUA in THF solution, there is no free C=O for OUA in DMSO solution, which indicates that the S=O of DMSO serves as an effective hydrogen-bond acceptor unit among OUA chains, capturing any free C=O. Figure S4c,d shows that in OUA-THF solution, free C=O exists; this is because THF disperses and blocks the interaction of OUA chains. Moreover, in the solid state, a small percentage of free C=O was observed because most OUA chains stack and form many H bonds. These results prove that DMSO is very important in making full use of free C=O units to build a tightly hydrogen-bonded network in OUA-gel.

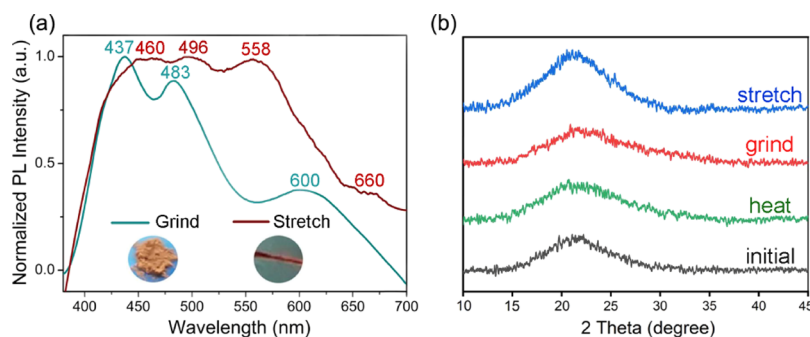


Figure 2. (a) Emission spectra of OUA-gel under grinding and stretching ($\lambda_{\text{ex}} = 302$ nm). (b) WAXD spectra of OUA-gel in the initial/heat/grind/stretch states.

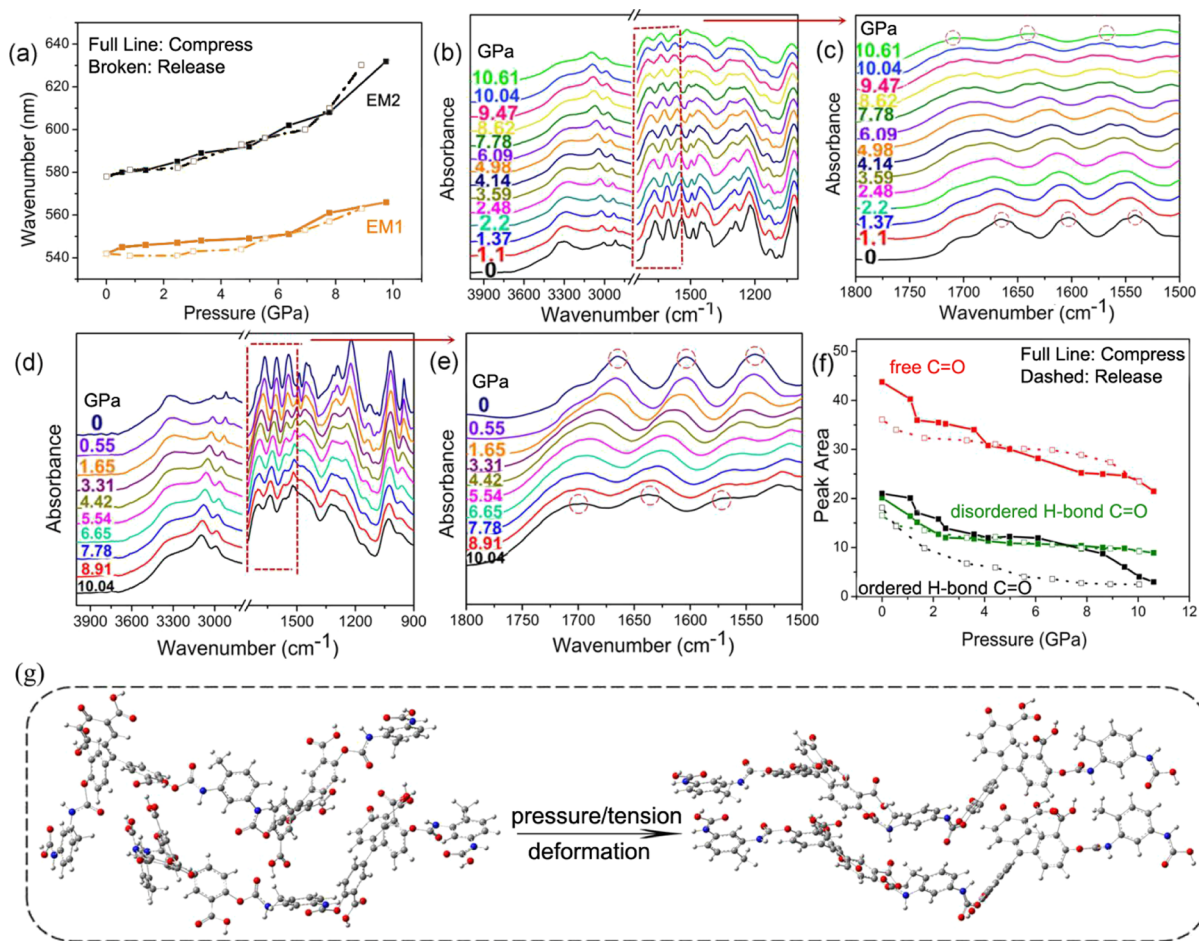


Figure 3. (a) Change in location of the PL of OUA-gel under compression and releasing. (b) Pressure-dependent FTIR spectra of OUA-gel under compression. (c) Expanded spectra of (b) in the selected region. (d) Pressure-dependent FTIR spectra of OUA-gel under releasing. (e) Expanded spectra of (d) in the selected region. (f) Change in FTIR peak areas of free/disordered/ordered hydrogen-bonded C=O for OUA-gel as a function of compression and releasing. (g) Proposed molecular models showing distortion of OUA-gel molecular chain under high pressure or tension.

OUA-gel is brightly fluorescent under UV illumination. At different excitation wavelengths, the PL spectra demonstrate different peak positions, with similar multiplex profiles, with maxima at 415/485 and 437/524/585 nm for $\lambda_{\text{ex}} = 302$ and 365 nm, respectively (Figure S5a). The multiple emission peaks suggest the presence of various emissive species, derived from different structures owing to chain folding and aggregation. The broad UV-vis absorption spectra of OUA-gel (Figure S5b) further suggested the possibility of multiple emission regions. It is proposed that different packing of these aggregates may cause significant impact on the emission behavior of OUA-gel. Indeed, Figure 2a shows polychromatic emission under different mechanical stimuli. After grinding, OUA-gel shows yellow emission, with peaks at 437/483/600 nm. For the amorphous chains, the cross-linking network collapses under mechanical stimuli and the twisted molecular chains are forced into a more planar conformation, which increases the effective conjugation length (ECL) resulting in red-shifted emission. However, after stretching, OUA-gel shows further red-shifted emission, with broad peaks at 460/496/558/660 nm. This can be explained as follows: a low shear rate force (stretching) gives the original twisted and entangled chains enough time and space to extend to promote the overall intrachain order (planarity) and conjugation lengths. However, the high shear rate force (grinding) does not allow the chains

to fully extend, and reduced deformation of the chains results in a more limited change in the intrachain conformational order, thus only minor red-shifted emission changes are observed upon grinding. Therefore, different color changes are produced by grinding and by stretching (Figure 2a and Supporting Information Movie).

This clear qualitative visualization of mechanical stress that has been easily achieved through the luminescence change of a single material is very rare. In order to explore the origin of this phenomenon, further studies were conducted on OUA-gel. Specifically, multiple hydrogen-bond connections are present between adjacent chains in OUA-gel, which further rigidify the molecular conformations; thus, OUA-gel has bright green emission in the original as-synthesized state. Meanwhile, the presence of many cavities in the OUA-gel makes the molecular chains highly stretchable and compressible. Upon grinding or stretching, while intermolecular interactions are destroyed, the molecules are also forced to adopt less-twisted conformations, thus giving red-shifted emissions. The mechanochromism of OUA-gel suggests that the emission color of OUA-gel can be modulated through tuning its conformation. This is further verified by the multicolor emission behavior of OUA-gel at different temperatures because hydrogen bonding is sensitive to temperature. Upon heating, OUA-gel exhibits emissions centered at 497 (at 275 K), 614 (at 303 K), and 654 nm (at

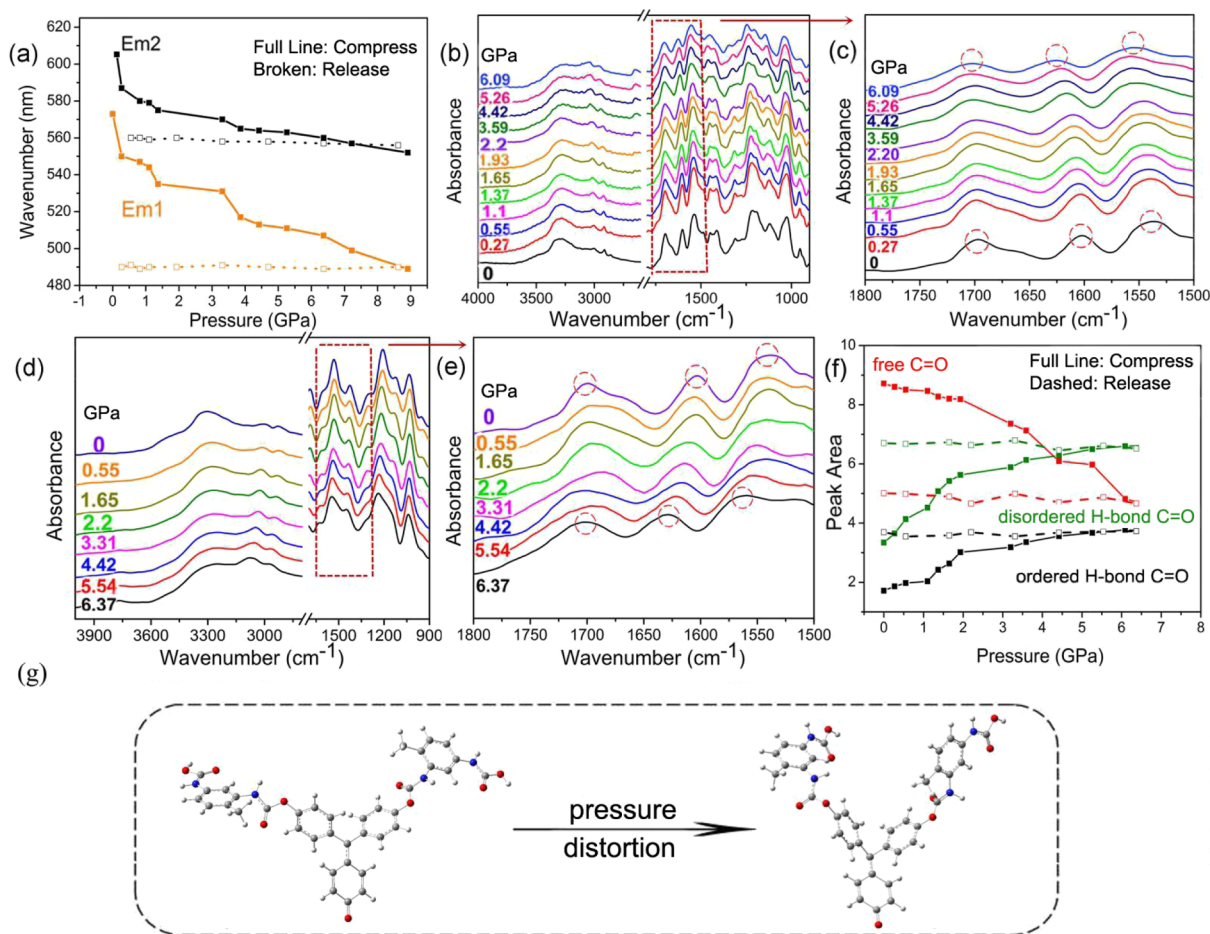


Figure 4. (a) Change in the PL of **OUR-gel** under compression and releasing. (b) Pressure-dependent FTIR spectra of **OUR-gel** under compression. (c) Enlarged spectra of (b) in the selected region. (d) Pressure-dependent FTIR spectra of **OUR-gel** under releasing. (e) Enlarged spectra of (d) in the selected region. (f) Change in FTIR peak areas of free/disordered/ordered hydrogen-bonded C=O for **OUR-gel** as a function of compression and releasing. (g) Proposed molecular models showing increased twist of **OUR-gel** molecular chain under high pressure.

325 K) (Figure S6) because of the varied conformations. Heating leads to the breaking of H bonds and weaker interactions among chains. These factors cause the micro-environment of **OUA-gel** to transform from amorphous to crystalline, accompanied by the considerable increase in the ECL and red-shifted emission.

Wide-angle X-ray diffraction (WAXD) was used to investigate the change in the crystallization rate of **OUA-gel** during heating, grinding, or stretching. As shown in Figure 2b, the peak at 2θ around 21.5° corresponds to the OU skeleton, as reported before.⁴⁰ **OUA-gel** shows a broad peak with varied intensity and width, suggesting that crystalline and amorphous microstructures exist simultaneously. In the initial state, OUA chains are relatively distorted and coiled. Interestingly, the intensity of the diffraction peak after stretching was greatly enhanced because slow stretching force, relative to quick grinding force, allows enough time and space for coiled OUA chains to straighten. Most of the disordered amorphous chains transform to an ordered crystalline conformation with increased conjugation length after stretching. In contrast, grinding could only induce a limited structural transformation and broaden the diffraction peak (without increasing its intensity) which is consistent with the PL results discussed above. After heating, Figure 2b shows that the diffraction peak broadens, indicating that the H bonds between the OUA chains break because of their thermal

sensitivity. The differential scanning calorimetry (DSC) curve of **OUA-gel** reveals a glass transition temperature (T_g) at 28°C during heating (Figure S7) and a reversible exothermic peak at 2.5°C during cooling, which is consistent with the thermochromic PL results shown in Figure S6.

To further investigate the origin of the mechanically sensitive chromogenic effect of **OUA-gel**, the influence of high pressure on the photophysical properties of **OUA-gel** and **OUR-gel** was studied by high-pressure fluorescence and FTIR experiments. Figures 3a and S8a show the PL spectra of **OUA-gel** upon compression in the range 0–9.76 GPa. Under ambient conditions, two emission bands were centered at 541 and 577 nm. As the pressure increased, the initial emissions underwent a gradual red shift with a decrease in PL intensity, and **OUA-gel** exhibited an ultrasensitive PL response even at an external pressure of 0.55 GPa. Moreover, the emission intensity of **OUA-gel** was preserved to a significant extent (Em1: 10.3%, Em2: 12.7%) when the pressure increased up to 9.76 GPa, suggesting excellent high-pressure resistance (Figure S8a). Importantly, previous gel systems mostly sense only low-pressure, including liquid gel films,⁴¹ piezo-resistive pressure sensors,⁴² and gel field-effect transistors.⁴³ Upon the complete release of pressure, the original peak positions and intensities before compression were observed again, indicating the pressure-related reversibility of **OUA-gel** as a consequence of the deforming space in the **OUA-gel** (Figures 3a and S8b).

To examine the effect of hydrogen bonding on the optical properties of **OUA-gel** under high pressure, pressure-dependent infrared absorption data were obtained at room temperature (Figure 3b–f). These data probe the hydrogen-bonded low-frequency vibrational modes ($1752\text{--}1500\text{ cm}^{-1}$) associated with free/disordered H-bonded/ordered H-bonded $\text{C}=\text{O}$ groups. With an increase in pressure, these vibrational modes undergo an obvious red shift, which is associated with the gradual reduction of van der Waals forces and H-bonding interactions. Additionally, all the vibrational bands change in width and weaken in intensity. Figure 3f shows the change in peak areas of free/disordered H-bonded/ordered H-bonded $\text{C}=\text{O}$ groups during compression and release processes, which relate to changes of H-bond strengths. The gradual and reversible change in conformation of **OUA-gel** during compression and release processes suggests there are deforming spaces in the **OUA-gel** network. The almost reversible process means that high pressure could temporarily disrupt H bonds and other intermolecular interactions in **OUA-gel**. However, all of the interactions gradually recover when the applied pressure is released.

Based on these observations, structural models of **OUA-gel** were proposed and optimized by Gaussian. Inter-/intramolecular hydrogen bonding within **OUA-gel** was established and possible changes in behavior are predicted by simulations. As a result of the propeller-shaped aurintricarboxylic acid and the 2,4-tolylene diisocyanate (TDI) units with a twist induced by the $-\text{CH}_3$ group and the rigidity of both of these units, the **OUA-gel** chains are distorted from planarity. Moreover, in the gel state, the twisted chains are surrounded by DMSO molecules, intermolecular van der Waals interactions, inter-/intramolecular hydrogen bonding from **OUA**–**OUA** and **OUA**–**DMSO** ensuring relatively entangled amorphous regions (Figure S9). When pressure is applied, the molecules tend to planarize to a more ordered crystalline state, and the conjugation length was extended, leading to a gradual red shift of luminescence. Moreover, a tight H-bonded network could offer additional elastic resistance to undertake and consume pressure and serve as a strain buffer layer. When the pressure was released, the interaction among chains is gradually recovered, and the molecular conformation reverts to a disordered amorphous state. Thus, both the intensity and peak position of luminescence recovered after removing pressure (Figure 3g). This is reversible mechanically chromogenic behavior. The coupling of the state of the molecular chains and fluorescence sensitivity of conformation with the mechanical stress makes it possible to observe and predict the microscopic conformational changes in the soft material.

For **OUR-gel**, under ambient conditions, two emissions are centered at 573 nm (shoulder) and 605 nm (Figures 4a and S10a). As the applied pressure was increased, the fluorescence clearly showed a decrease in intensity, with a gradual blue shift in the position of the peaks, which is opposite from **OUA-gel**. Application of pressure up to 8.91 GPa caused a noticeable change in peak position of **OUR-gel** (Em1: from 573 to 494 nm; Em2: from 605 to 547 nm; as shown in Figure 4a). The emission of **OUR-gel** retained a significant amount of its original intensity (Em1: 6.2%, Em2: 5.4%) at 8.91 GPa, showing good resistance to high pressure (Figure S10a), which is similar to **OUA-gel**. As the applied pressure was released from 8.91 to 0 GPa, the positions of the emission peaks of **OUR-gel** were almost unchanged, although the intensity was

recovered, which is markedly different from traditional piezochromic behavior.

Piezochromic materials often undergo a complete or partially reversible phase/color transition when the pressure is fully released.^{44–47} Accordingly, the color change of **OUR-gel** under pressure is irreversible. This fact was further testified by an irreversible FTIR spectrum (Figure 4b–f). Interestingly, the content of disordered and ordered hydrogen-bonded $\text{C}=\text{O}$ bonds increased. In contrast, the content of free $\text{C}=\text{O}$ decreased, which means more hydrogen bonds would form upon applying pressure, resulting in a tighter cross-linking and consequently a shortened ECL; therefore, **OUR-gel** emits bluer light (Figure 4g). The irreversible process means that high pressure could destroy H bonds and other intermolecular interaction among **OUR-gel** molecules. These bonds and interactions could not recover even upon releasing the applied pressure.

Based on the abovementioned results, models of the structural change of **OUR-gel** were optimized by Gaussian. Because of a lack of the key carboxyl groups present in **OUA-gel**, only limited cross-linking H bonds are formed among **OUR**–**OUR** and **OUR**–**DMSO** in **OUR-gel** (Figure S11). Thus, under applied pressure, **OUR-gel** transformed to a more twisted conformation, leading to a gradual blue shift of luminescence and the original conformation did not recover after releasing the pressure (Figure 4g). This is consistent with the observation that **OUR-gel** does not show multicolored behavior.

A calibration sensing curve of the PL feature of **OUR-gel** against pressure is described. The importance of incorporating sufficient H-bonding motifs for variable and reversible optical properties has been proved by comparing the high-pressure experiments of **OUA-gel** and **OUR-gel**. The appropriate H-bonding motifs mean that **OUR-gel** retains a fixed conformation and peak location even after the applied pressure is removed. This unusual property could be used as a pressure sensor, especially under limited test conditions, which can operate without instant data signal processing and can be analyzed slowly after sampling. As shown in Figure 4a, the fluorescence properties as a function of pressure can be quantified using the calibration curve. With increasing pressure, the ratio of Em2 to Em1 increases (Figure 5). Multiparameter (peaks) sensing improves the accuracy. The ratio of Em2 to Em1 was plotted to highlight how FTIR spectroscopy on **OUR-gel** can be used to direct and

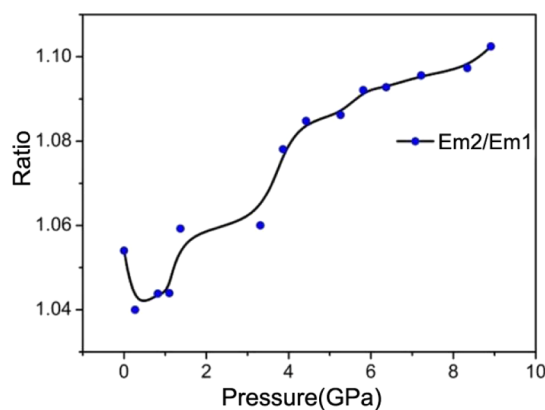


Figure 5. Ratio of Em2 to Em1 of **OUR-gel** as a function of pressure is determined from the sensor calibration given in Figure 4a.

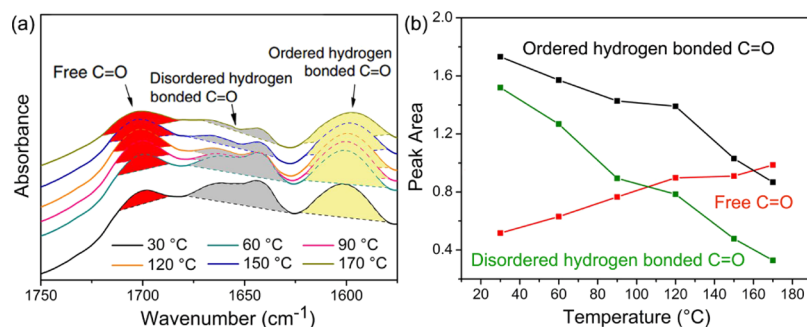


Figure 6. (a) Variable-temperature FTIR spectra of **OUA-gel** in the 1750–1550 cm^{-1} region. (b) Change in FTIR peak areas of free/disordered/ordered hydrogen-bonded C=O for **OUA-gel** as a function of temperature.

noninvasively detect the material's conformation under different pressures. The changeable interaction in **OUR-gel**, resulting in distinct vibronic fingerprints, allows sensitive and quantitative detection of how interactions in a soft gel material lead to changes in the conformation of a single oligomer chain.

The mechanism of supramolecular cross-linking of **OUA-gel** with multiple hydrogen-bonding interactions was also explored by variable-temperature ^1H NMR and FTIR spectra. In Figure S12, at 30 $^{\circ}\text{C}$, the NH protons of the imino group were observed at 9.10, 8.50, and 7.90 ppm. However, at 80 $^{\circ}\text{C}$, those NH protons shifted upfield to 8.82, 8.30, and 7.85 ppm, respectively, and broadened, demonstrating that the intermolecular hydrogen bonds were largely dissociated at the higher temperature.⁴⁷ Figures 6 and S13 show the variable-temperature FTIR spectra of **OUA-gel**. The peaks in the range from 1725 to 1575 cm^{-1} , attributed to different types of C=O bonds, were further studied by peak differentiating and integration of the peak areas.³⁴ As shown in Figure 6a, there are three distinct carbonyl stretching bands in different environments: free C=O at 1700 cm^{-1} , disordered hydrogen-bonded C=O at 1650 cm^{-1} , and ordered hydrogen-bonded C=O at 1600 cm^{-1} . The latter two are assigned to H-bonded cross-links between the chains of the **OUA-gel**. Figure 6b shows the changes in peak areas of these three C=O environments as a function of temperature. The peak areas at 1650 and 1600 cm^{-1} decreased and shifted to longer wavenumbers with increasing temperature, illustrating that the content of both disordered and ordered hydrogen-bonded C=O bonds decreased. However, in contrast, the broad peak near 1700 cm^{-1} from free C=O gradually shifted to lower wavenumbers and increased in area. This result means that the interchain hydrogen bonds were broken upon heating, and then, free C=O units were gradually released from ordered/disordered hydrogen-bonded C=O units, resulting in a decrease in the cross-linking density and causing spatial extension of oligomer segments to dissipate energy.

According to the abovementioned results, the mechanically induced chromogenic properties are ascribed to a rich array of multiple H bonds, as visualized schematically in Figure 7. Initially, **OUA** chains adopt a highly twisted and entangled state because of multiple H bonds and other noncovalent forces. When subjected to an external force, the close-knit superstructure is broken, and the chains open; thus, the emission of **OUA-gel** changes (Figure 7a). The number ratio of DMSO and **OUA** molecules in the **OUA-gel** matrix was calculated according to the feed ratio. A schematic diagram was then plotted (Figure 7b) for a hydrogen-bonded network, according to the number ratio of DMSO/**OUA** = 10.68:1. Six

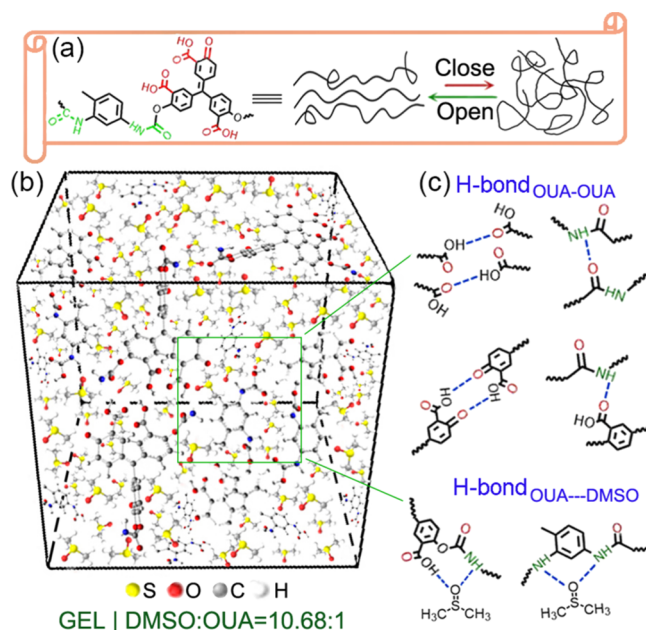


Figure 7. Schematic illustration to explain the chromogenic properties in **OUA-gel**. (a) Chain entanglement and opening of **OUA**. (b) Schematic diagram of the **OUA-gel** matrix. (c) Multiple types of hydrogen bonds within the **OUA-gel** matrix.

types of hydrogen bonds exist in the network including the self-complementary H bonds of carboxyl groups, H bonds from urethane amide groups with carboxyl groups or carbonyl groups, and H bonds between the sulfoxide unit of DMSO molecules among the gel matrix with urethane amide groups or carboxyl groups (Figure 7c).

Comparing **OUA-gel** with **OUR-gel**, we conclude that aurintricarboxylic acid provides H bonds and spacial twisting, both of which are vital for the mechanical chromogenic property. Additionally, the main chain should be short, as observed in the present oligomers: a longer chain may be too soft and flexible, lacking enough hardness to keep a highly twisted state.

CONCLUSIONS

To achieve a multifunctional and mechanochromic soft material, propeller-like aurintricarboxylic acid with sterically crowded and twisted conformations was inserted into the main chain of an oligourethane derivative. This structure benefits the emission by avoiding π - π stacking between aromatic rings. Specifically, in a supramolecular gel matrix, multiple H-

bonding intermolecular interactions tightly rigidify the conformations of the molecular chains, thus endowing OUA-gel with a highly twisted conformation. OUA-gel shows tunable multicolor mechanochromism upon mechanical stimuli. Notably, it is the first example of an oligourethane that exhibits multicolored emission through mild mechanical force. Our studies contribute to fundamental research on the interplay between local conformations and luminescent properties of gels, with potential practical applications in optical shear and/or pressure-sensing devices.

EXPERIMENTAL SECTION

General Information. Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. ^1H NMR spectra were recorded at 25 °C on a Varian 500 MHz spectrometer and were referenced internally to the residual proton resonance in DMSO- d_6 (δ 2.5 ppm). The molecular weights of the oligomers were calculated by gel permeation chromatography (GPC) analysis carried out on a Waters 515–2410 system using polystyrene standards as the molecular weight reference and dimethylsulfoxide as the eluent. UV–vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrophotometer. FTIR spectra were obtained using a Nicolet 6700 FT/IR spectrophotometer. Variable-temperature FTIR experiments were performed on a Bruker Tensor 27 FTIR spectrophotometer with a Eurotherm 2404 temperature controller. AFM images were obtained using a Digital Instrument Multimode Nanoscope IIID. DSC data were obtained using a NETZSCH thermal analysis DSC200 F3 instrument under argon with a heating rate of 10 °C min $^{-1}$. WAXD patterns of the samples were collected on a Rigaku Dmax 2000 instrument.

Synthesis of Oligourethane Gels. OUA-Gel. Aurintricarboxylic acid (2.62 mmol), DABCO (0.105 mmol), anhydrous THF (2 mL), and DMSO (2 mL) were added to a dried two-neck round-bottom flask and then stirred at room temperature for 10 min under a nitrogen atmosphere. Then, tolylene-2,4-diisocyanate (TDI) (2.73 mmol; NCO/OH molar ratio ca. 1.04) was added and the mixture was heated at 90 °C for 8 h under a nitrogen atmosphere (a slight excess of the –NCO reagent was used to ensure that the aurintricarboxylic acid monomer reacted completely). Finally, the resulting sticky oligourethane gel OUA-gel was obtained and stored in a freezer. IR (KBr): ν = 3613 cm $^{-1}$ (–OH), 3325 cm $^{-1}$ (N–H), 2964 and 2891 cm $^{-1}$ (–CH $_2$ – asymmetric and symmetric stretch), 1718 and 1754 cm $^{-1}$ (free and H-bond C=O). ^1H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 11.61 (broad, 3H; –COOH), 9.06/8.50/8.23, (s, 2H; –NH), 8.08–7.86 (broad, 1H), 8.81–8.57 (broad, 4H), 7.56–7.33 (broad, 2H), 7.31–6.97 (broad, 4H), 6.94–6.68 (broad, 4H), 6.68–6.34 (broad, 1H), 2.27–1.92 (broad, 6H). M_w = 3162 g mol $^{-1}$.

OUR-Gel. The synthetic procedure for OUR-gel was the same as OUA-gel, except that monomer rosolic acid (2.62 mmol) was used instead of aurintricarboxylic acid. The resulting sticky oligourethane gel OUR-gel was obtained and stored in a freezer. IR (KBr): ν = 3433 cm $^{-1}$ (N–H), 3001 and 2913 cm $^{-1}$ (–CH $_2$ – asymmetric and symmetric stretch), 1656 cm $^{-1}$ (C=O). ^1H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 8.95/8.47/8.22, (s, 2H; –NH), 8.02–7.96 (broad, 1H), 7.84–7.66 (broad, 4H), 7.48–7.35 (broad, 2H), 7.28–6.97 (broad, 4H), 6.90–6.62 (broad, 4H), 6.54–6.23 (broad, 1H), 2.25–1.95 (broad, 6H). M_w = 2882 g mol $^{-1}$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01620>.

Additional structural characterization and photophysical properties (PDF)

Supplementary movie (MP4)

AUTHOR INFORMATION

Corresponding Authors

Dongxia Zhu – Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China; Email: zhudx047@nenu.edu.cn

Bing Li – College of Physics, Changchun Normal University, Changchun 130032, China; Email: libing@ccsfu.edu.cn

Martin R. Bryce – Department of Chemistry, Durham University, Durham DH1 3LE, U.K.; orcid.org/0000-0003-2097-7823; Email: m.r.bryce@durham.ac.uk

Authors

Nan Jiang – Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China

Shi-Hao Ruan – State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, P. R. China

Xing-Man Liu – Key Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.chemmater.0c01620>

Author Contributions

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REFERENCES

- (1) Ferrara, M.; Bengisu, M. *Materials that Change Color: Smart Materials, Intelligent Design*; Springer Briefs in Applied Sciences and Technology Series; Springer: Heidelberg, 2014; pp 9–60.
- (2) Li, J.; Nagamani, C.; Moore, J. S. Polymer Mechanochemistry: From Destructive to Productive. *Acc. Chem. Res.* **2015**, *48*, 2181–2190.
- (3) Kosuge, T.; Zhu, X.; Lau, V. M.; Aoki, D.; Martinez, T. J.; Moore, J. S.; Otsuka, H. Multicolor Mechanochromism of a Polymer/Silica Composite with Dual Distinct Mechanophores. *J. Am. Chem. Soc.* **2019**, *141*, 1898–1902.
- (4) Kim, J.-H.; Jung, Y.; Lee, D.; Jang, W.-D. Thermoresponsive Polymer and Fluorescent Dye Hybrids for Tunable Multicolor Emission. *Adv. Mater.* **2016**, *28*, 3499–3503.

- (5) Ahn, H.; Hong, J.; Kim, S. Y.; Choi, I.; Park, M. J. A pH-Responsive Molecular Switch with Tricolor Luminescence. *ACS Appl. Mater. Interfaces* **2015**, *7*, 704–712.
- (6) Beiermann, B. A.; Kramer, S. L. B.; Moore, J. S.; White, S. R.; Sottos, N. R. Role of Mechanophore Orientation in Mechanochemical Reactions. *ACS Macro Lett.* **2012**, *1*, 163–166.
- (7) Lee, C. K.; Beiermann, B. A.; Silberstein, M. N.; Wang, J.; Moore, J. S.; Sottos, N. R.; Braun, P. V. Exploiting Force Sensitive Spiropyrans as Molecular Level Probes. *Macromolecules* **2013**, *46*, 3746–3752.
- (8) Nian, H.; Li, A.; Li, Y.; Cheng, L.; Wang, L.; Xu, W.; Cao, L. Tetraphenylethene-based tetracationic dicyclopentanes: synthesis, mechanochromic luminescence, and photochemical reactions. *Chem. Commun.* **2020**, *56*, 3195–3198.
- (9) Calvino, C.; Guha, A.; Weder, C.; Schrettl, S. Self-Calibrating Mechanochromic Fluorescent Polymers Based on Encapsulated Excimer-Forming Dyes. *Adv. Mater.* **2018**, *30*, 1704603.
- (10) Benito, Q.; Le Goff, X. F.; Maron, S.; Fargues, A.; Garcia, A.; Martineau, C.; Taulelle, F.; Kahlal, S.; Gacoin, T.; Boilot, J.-P.; Perruchas, S. Polymorphic Copper Iodide Clusters: Insights into the Mechanochromic Luminescence Properties. *J. Am. Chem. Soc.* **2014**, *136*, 11311–11320.
- (11) Butler, T.; Morris, W. A.; Samonina-Kosicka, J.; Fraser, C. L. Mechanochromic Luminescence and Aggregation Induced Emission of Dinaphthoylemethane β -Diketones and Their Boronated Counterparts. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1242–1251.
- (12) Chan, E. P.; Walish, J. J.; Urbas, A. M.; Thomas, E. L. Mechanochromic Photonic Gels. *Adv. Mater.* **2013**, *25*, 3934–3947.
- (13) Yang, D.; Ye, S.; Ge, J. From Metastable Colloidal Crystalline Arrays to Fast Responsive Mechanochromic Photonic Gels: An Organic Gel for Deformation-Based Display Panels. *Adv. Funct. Mater.* **2014**, *24*, 3197–3205.
- (14) Cingil, H. E.; Storm, I. M.; Yorulmaz, Y.; te Brake, D. W.; de Vries, R.; Cohen Stuart, M. A.; Sprakel, J. Monitoring Protein Capsid Assembly with a Conjugated Polymer Strain Sensor. *J. Am. Chem. Soc.* **2015**, *137*, 9800–9803.
- (15) Zhao, H.; Prieto-López, L. O.; Zhou, X.; Deng, X.; Cui, J. Multistimuli Responsive Liquid-Release in Dynamic Polymer Coatings for Controlling Surface Slipperiness and Optical Performance. *Adv. Mater. Interfaces* **2019**, *6*, 1901028.
- (16) Yanagisawa, Y.; Nan, Y.; Okuro, K.; Aida, T. Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking. *Science* **2018**, *359*, 72–76.
- (17) Song, L.; Zhu, T.; Yuan, L.; Zhou, J.; Zhang, Y.; Wang, Z.; Tang, C. Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures. *Nat. Commun.* **2019**, *10*, 1315.
- (18) Beyer, M. K.; Clausen-Schaumann, H. Mechanochemistry: The Mechanical Activation of Covalent Bonds. *Chem. Rev.* **2005**, *105*, 2921–2948.
- (19) Jiang, S.; Zhang, L.; Xie, T.; Lin, Y.; Zhang, H.; Xu, Y.; Weng, W.; Dai, L. Mechanoresponsive PS-PnBA-PS Triblock Copolymers via Covalently Embedding Mechanophore. *ACS Macro Lett.* **2013**, *2*, 705–709.
- (20) Crenshaw, B. R.; Burnworth, M.; Khariwala, D.; Hiltner, A.; Mather, P. T.; Simha, R.; Weder, C. Deformation-Induced Color Changes in Mechanochromic Polyethylene Blends. *Macromolecules* **2007**, *40*, 2400–2408.
- (21) Kosuge, T.; Zhu, X.; Lau, V. M.; Aoki, D.; Martinez, T. J.; Moore, J. S.; Otsuka, H. Multicolor Mechanochromism of a Polymer/Silica Composite with Dual Distinct Mechanophores. *J. Am. Chem. Soc.* **2019**, *141*, 1898–1902.
- (22) Filonenko, G. A.; Sun, D.; Weber, M.; Müller, C.; Pidko, E. A. Multicolor Organometallic Mechanophores for Polymer Imaging Driven by Exciplex Level Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 9687–9692.
- (23) McFadden, M. E.; Robb, M. J. Force-Dependent Multicolor Mechanochromism from a Single Mechanophore. *J. Am. Chem. Soc.* **2019**, *141*, 11388–11392.
- (24) Li, C.; Zhang, Y.; Hu, J.; Cheng, J.; Liu, S. Reversible Three-State Switching of Multicolor Fluorescence Emission by Multiple Stimuli Modulated FRET Processes within Thermoresponsive Polymeric Micelles. *Angew. Chem., Int. Ed.* **2010**, *49*, 5120–5124.
- (25) Matsubara, K.; Watanabe, M.; Takeoka, Y. A Thermally Adjustable Multicolor Photochromic Hydrogel. *Angew. Chem., Int. Ed.* **2007**, *46*, 1688–1692.
- (26) Klukovich, H. M.; Kean, Z. S.; Iacono, S. T.; Craig, S. L. Mechanically Induced Scission and Subsequent Thermal Remending of Perfluorocyclobutane Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 17882–17888.
- (27) Wu, Y.; Hu, J.; Huang, H.; Li, J.; Zhu, Y.; Tang, B.; Han, J.; Li, L. Memory Chromic Polyurethane with Tetraphenylethylene. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 104–110.
- (28) Ishizuki, K.; Aoki, D.; Goseki, R.; Otsuka, H. Multicolor Mechanochromic Polymer Blends That Can Discriminate between Stretching and Grinding. *ACS Macro Lett.* **2018**, *7*, 556–560.
- (29) Crenshaw, B. R.; Weder, C. Self-Assessing Photoluminescent Polyurethanes. *Macromolecules* **2006**, *39*, 9581–9589.
- (30) Dong, Y.; Zhang, J.; Tan, X.; Wang, L.; Chen, J.; Li, B.; Ye, L.; Xu, B.; Zou, B.; Tian, W. Multi-stimuli responsive fluorescence switching: the reversible piezochromism and protonation effect of a divinylanthracene derivative. *J. Mater. Chem. C* **2013**, *1*, 7554–7559.
- (31) Sagara, Y.; Karman, M.; Verde-Sesto, E.; Matsuo, K.; Kim, Y.; Tamaoki, N.; Weder, C. Rotaxanes as Mechanochromic Fluorescent Force Transducers in Polymers. *J. Am. Chem. Soc.* **2018**, *140*, 1584–1587.
- (32) Sharma, R. K.; Garg, B. S.; Kurosaki, H.; Goto, M.; Otsuka, M.; Yamamoto, T.; Inoue, J.-i. Aurine tricarboxylic acid, a potent metal-chelating inhibitor of NF κ B-DNA binding. *Bioorg. Med. Chem.* **2000**, *8*, 1819–1823.
- (33) Song, Y.; Liu, Y.; Qi, T.; Li, G. L. Towards Dynamic but Supertough Healable Polymers through Biomimetic Hierarchical Hydrogen-Bonding Interactions. *Angew. Chem., Int. Ed.* **2018**, *57*, 13838–13842.
- (34) Zhang, H.; Wu, Y.; Yang, J.; Wang, D.; Yu, P.; Lai, C. T.; Shi, A. C.; Wang, J.; Cui, S.; Xiang, J.; Zhao, N.; Xu, J. Superstretchable Dynamic Polymer Networks. *Adv. Mater.* **2019**, *31*, 1904029.
- (35) Yan, X.; Liu, Z.; Zhang, Q.; Lopez, J.; Wang, H.; Wu, H.-C.; Niu, S.; Yan, H.; Wang, S.; Lei, T.; Li, J.; Qi, D.; Huang, P.; Huang, J.; Zhang, Y.; Wang, Y.; Li, G.; Tok, J. B.-H.; Chen, X.; Bao, Z. Quadruple H-Bonding Cross-Linked Supramolecular Polymeric Materials as Substrates for Stretchable, Antitearing, and Self-Healable Thin Film Electrodes. *J. Am. Chem. Soc.* **2018**, *140*, 5280–5289.
- (36) Song, P.; Wang, H. High-Performance Polymeric Materials through Hydrogen-Bond Cross-Linking. *Adv. Mater.* **2020**, *32*, 1901244.
- (37) Feula, A.; Tang, X.; Giannakopoulos, I.; Chippindale, A. M.; Hamley, I. W.; Greco, F.; Paul Buckley, C.; Siviour, C. R.; Hayes, W. An adhesive elastomeric supramolecular polyurethane healable at body temperature. *Chem. Sci.* **2016**, *7*, 4291–4300.
- (38) Guan, Z.; Roland, J. T.; Bai, J. Z.; Ma, S. X.; McIntire, T. M.; Nguyen, M. Modular Domain Structure: A Biomimetic Strategy for Advanced Polymeric Materials. *J. Am. Chem. Soc.* **2004**, *126*, 2058–2065.
- (39) Jiang, N.; Zhu, D.; Su, Z.; Bryce, M. R. Blue-emitting thermoreversible oligourethane gelators with aggregation-induced emission properties. *J. Mater. Chem. C* **2020**, *8*, 5137–5142.
- (40) Jiang, N.; Li, G.-F.; Zhang, B.-H.; Zhu, D.-X.; Su, Z.-M.; Bryce, M. R. Aggregation-Induced Long-Lived Phosphorescence in Non-conjugated Polyurethane Derivatives at 77 K. *Macromolecules* **2018**, *51*, 4178–4184.
- (41) Zhang, S.; Wang, F.; Peng, H.; Yan, J.; Pan, G. Flexible Highly Sensitive Pressure Sensor Based on Ionic Liquid Gel Film. *ACS Omega* **2018**, *3*, 3014–3021.
- (42) Lee, J.; Kim, J.; Shin, Y.; Jung, I. Ultra-robust wide-range pressure sensor with fast response based on polyurethane foam doubly coated with conformal silicone rubber and CNT/TPU nanocomposites islands. *Composites, Part B* **2019**, *177*, 107364.

- (43) Yamada, S.; Sato, T.; Toshiyoshi, H. A pressure sensitive ionic gel FET for tactile sensing. *Appl. Phys. Lett.* **2017**, *110*, 253501–253504.
- (44) Wu, J.; Cheng, Y.; Lan, J.; Wu, D.; Qian, S.; Yan, L.; He, Z.; Li, X.; Wang, K.; Zou, B.; You, J. Molecular Engineering of Mechanochromic Materials by Programmed C-H Arylation: Making a Counterpoint in the Chromism Trend. *J. Am. Chem. Soc.* **2016**, *138*, 12803–12812.
- (45) Wang, Y.; Tan, X.; Zhang, Y.-M.; Zhu, S.; Zhang, I.; Yu, B.; Wang, K.; Yang, B.; Li, M.; Zou, B.; Zhang, S. X.-A. Dynamic Behavior of Molecular Switches in Crystal under Pressure and Its Reflection on Tactile Sensing. *J. Am. Chem. Soc.* **2015**, *137*, 931–939.
- (46) Wang, L.; Wang, K.; Zou, B.; Ye, K.; Zhang, H.; Wang, Y. Luminescent Chromism of Boron Diketonate Crystals: Distinct Responses to Different Stresses. *Adv. Mater.* **2015**, *27*, 2918–2922.
- (47) Song, Y.; Liu, Y.; Qi, T.; Li, G. L. Towards Dynamic but Supertough Healable Polymers through Biomimetic Hierarchical Hydrogen-Bonding Interactions. *Angew. Chem., Int. Ed.* **2018**, *57*, 13838–13842.